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# **Evaluation of Low pH at Bear Canyon Lake, Arizona**

**A Case Study in “Natural Condition”**

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## SECTION I: BACKGROUND

### ***Water Quality Standards and Assessment***

Water quality standards are one of the cornerstones of the Clean Water Act and play a central role in the implementation of Arizona's water quality management programs. These standards define the water quality goals and designate the uses to be protected for Arizona's surface waters. They also prescribe the criteria necessary to maintain and protect water quality for the designated uses.

The Arizona Department of Environmental Quality (ADEQ) is required under section 305(b) of the Clean Water Act to report the status of surface water and ground water quality in Arizona. This report is referred to as Arizona's 305(b) report. Assessments are based on all readily available, credible, and scientifically defensible monitoring data received from many state, federal, and natural resource management programs. Waterbodies assessed as having impaired uses that require more than existing technology and permit controls to achieve or maintain water quality standards are listed on the 303(d) list.

### ***Listing***

The Environmental Protection Agency (EPA) added Bear Canyon Lake to Arizona's 2004 303(d) water quality impairment list for low pH. The phenomenon of low pH in lakes is rare in Arizona, as most reservoirs are well buffered. This report evaluates the occurrence of low pH in small headwater reservoirs, comparing land uses, morphology, geology, soils, vegetation and climatic patterns within the context of "natural condition" and designated use support. A case is made for de-listing Bear Canyon Lake citing A.A.C. R18.11.604.C(1): *"Pollutant loadings from naturally occurring conditions alone are sufficient to cause a violation of water quality standards."*

### ***Designated Uses***

Designated uses are based on the uses people and wildlife make of surface water. The State of Arizona sets narrative and numeric surface water standards for water quality based on these uses and are specified for individual surface waters. There are six groups of "designated uses" from which any number of uses may be applied to individual surface water. Bear Canyon Lake carries designated uses for Aquatic and Wildlife cold water (A&Wc), Full Body Contact (FBC), Fish Consumption (FC), Agriculture Livestock (AgL), and Agriculture Irrigation (Agl) (ADEQ, 2009). pH is a core parameter used in assessment of all but the FC use. The most stringent standard for pH, shared by both A&W cold and warm water uses and the FBC use, is a range from 6.5 SU to 9.0 SU.

### ***Water Quality Criteria for pH***

The *Water Quality Criteria* document of 1968 (Green Book) is primarily focused on recommending discharge limitations to surface water. The Green Book sets forth the following pH expectations for primary recreation (assumed under FBC) and protection of fresh water organisms (A&W):

*In primary contact recreation waters, the pH should be within the range of 6.5 – 8.3 except when due to natural causes and in no case shall be less than 5.0 nor more than 9.0. When the pH is less than 6.5 or more than 8.3, discharge of substances which further increases unfavorable total acidity or alkalinity should be limited.*

*.. Almost all natural waters have some buffer capacity. Therefore, to minimize eye irritation to bathers, it seems desirable to suggest that for natural waters with low buffer capacity, the pH range be between 5.0 and 9.0.*

*.. Some natural waters with a pH of 4 support fish and other organisms. In these cases the acidity is due primarily to carbon dioxide and humic acids and the water has little buffering capacity (low total alkalinity).*

Subsequent criteria documents followed the Green Book that further addressed ambient water quality criteria, the Blue Book in 1973, the Red Book in 1976, and the Gold Book in 1986. EPA regularly updates the criteria, which are now available on their web site.

The Red Book set the pH criteria for aquatic life chronic exposure that are still in place: 6.5 – 9.0 (EPA 440/9-76-023, July, 1976). This standard is a *Criterion Continuous Concentration (CCC)*, or an estimate of the highest concentration of a substance in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect. In support of the pH criteria range, the CCC for minimum alkalinity is 20 mg/L except where alkalinity is naturally lower, in which case the criterion cannot be lower than 25% of the natural level (EPA web site <http://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table>). The use of the 25 percent reduction avoids the problem of establishing standards on waters where natural alkalinity is at or below 20 mg/L. For such waters, alkalinity should not be further reduced.

The Gold Book cites a study published by the European Inland Fisheries Advisory Commission (1969):

*There is no definite pH range within which a fishery is unharmed and outside which it is damaged, but rather there is a gradual deterioration as the pH values are further removed from the normal range. The pH range which is not directly lethal to fish is 5 – 9; however, the toxicity of several common pollutants is markedly affected by pH changes within this range, and increasing acidity or alkalinity may make these poisons more toxic.*

[pH in the range of 5.0 – 6.0] is “unlikely to be harmful to any species unless either the concentration of free CO<sub>2</sub> is greater than 20 ppm, or the water contains iron salts which are precipitated as ferric hydroxide, the toxicity of which is unknown”. [mg CO<sub>2</sub>/L = 2.0\*bicarbonate\*10(6-pH) from SM4500-CO<sub>2</sub> D. Carbon Dioxide and Forms of Alkalinity by Calculation p 4-18]

However, the Gold Book also cites a bioassay study on the fathead minnow that recorded abnormal behavior and physiology at a pH value of 5.2, as well as reduced egg production and hatchability when the pH was less than 6.6. Additional bioassays on invertebrate nymphs supported the Red Book criteria range for pH of 6.5 – 9.0.

Heavy metals such as cadmium, lead, and chromium dissolve more easily in more acidic water (lower pH). This is important because many heavy metals also become much more toxic when dissolved in water. According to Spry and Wiener (1991):

*fish in low-alkalinity lakes having pH of 6.0-6.5 or less often have higher body or tissue burdens of mercury, cadmium, and lead than do fish in nearby lakes with higher pH. The greater bioaccumulation of these metals in such waters seems to result partly from the greater aqueous abundances of biologically available forms*

*[(CH<sub>3</sub>), Hg(+), Cd(2+), and Pb(2+)] at low pH. In addition, the low concentrations of aqueous calcium in low-alkalinity lakes increase the permeability of biological membranes to these metals, which in fish may cause greater uptake from both water and food.*

## SECTION II: BEAR CANYON LAKE

### Setting

Bear Canyon Lake is one of several reservoirs located along the Mogollon Rim in north central Arizona (Figure 1). This waterbody is among several small man-made reservoirs constructed by the Arizona Game and Fish Department (AGFD) for recreation in the late 1950s to late 1960s; Bear Canyon dam was built in 1964. The reservoir impounds approximately 60 surface acres, capturing runoff and snowmelt from a watershed of 1,241 acres. The ratio of the watershed to the lake is 20.7, which is quite small for a reservoir. According to the nearest Snow Telemetry (SNOTEL) station at Promontory Butte, the Rim area has experienced anywhere from 2.3 inches of precipitation as snow water equivalent in a dry year (2006), to over 80 inches in the wettest year on record (1985). The official median value for January 6 is 4 inches, the average seasonal accumulation (from 1981-2010) is 10.5 inches.

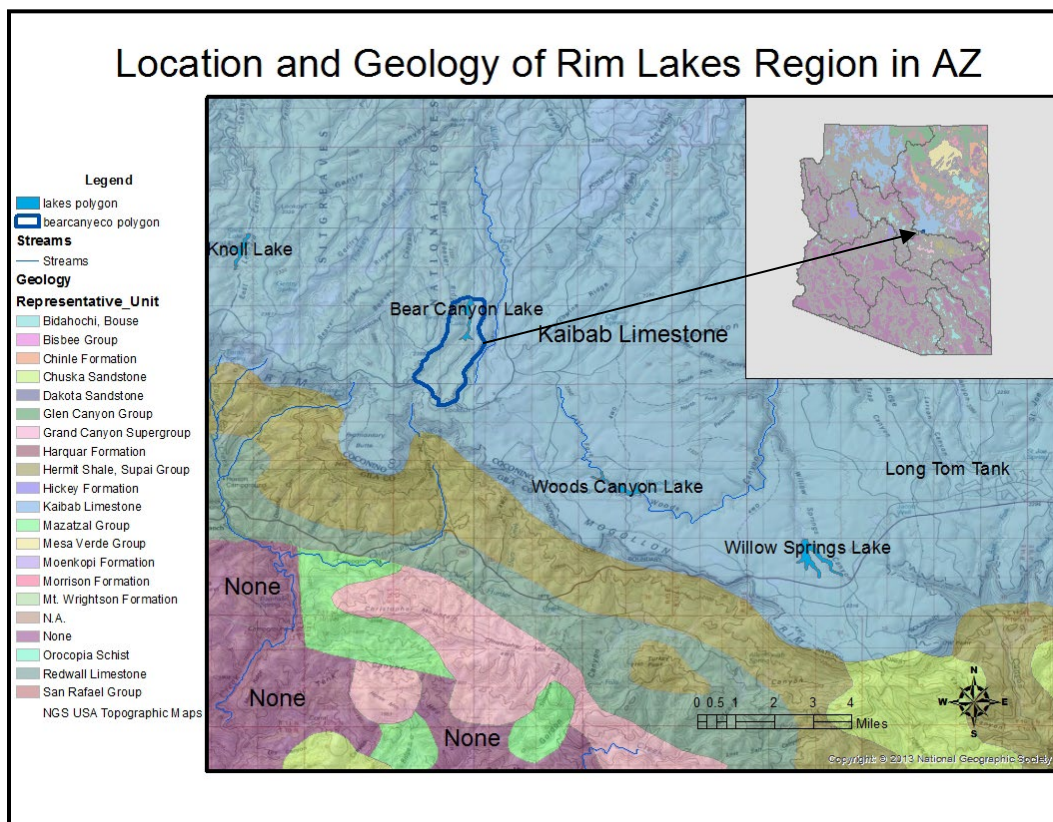


Figure 1. Vicinity Map of Bear Canyon Lake/Watershed and other Rim Lakes

Bear Canyon Lake, located near the edge of the Mogollon Rim in north-central Arizona, sits at an elevation of 7,560 feet in conifer forest. With a maximum depth of 45 feet, the lake is one of several popular fishing and camping destinations along the Rim in Coconino



County. The watershed of Bear Canyon Lake is managed by the Apache-Sitgreaves National Forest, while the AGFD stocks the lake with Rainbow Trout. According to the AGFD web site, *“Because of its depth, this lake has no water quality problems. The Department stocks it with catchable-sized rainbow trout about six times each year.*

The lake’s source of water is from snowmelt and two ephemeral drainages that contribute to the lake during storm events. There is no development in the Bear Canyon watershed aside from dirt roads and rustic campsites. The Forest Service maintains a campground near the lake that provides 30 campsites (tents only) and two nearby picnic grounds with a capacity of 328. There are no boat ramps at Bear Canyon Lake; boats must be carried down to the lake and motors must be electric. Access to the lake is limited to two trails and the shoreline is steep and narrow (Figure 2). Access is restricted in the winter when roads are closed due to snow, generally November to late April.

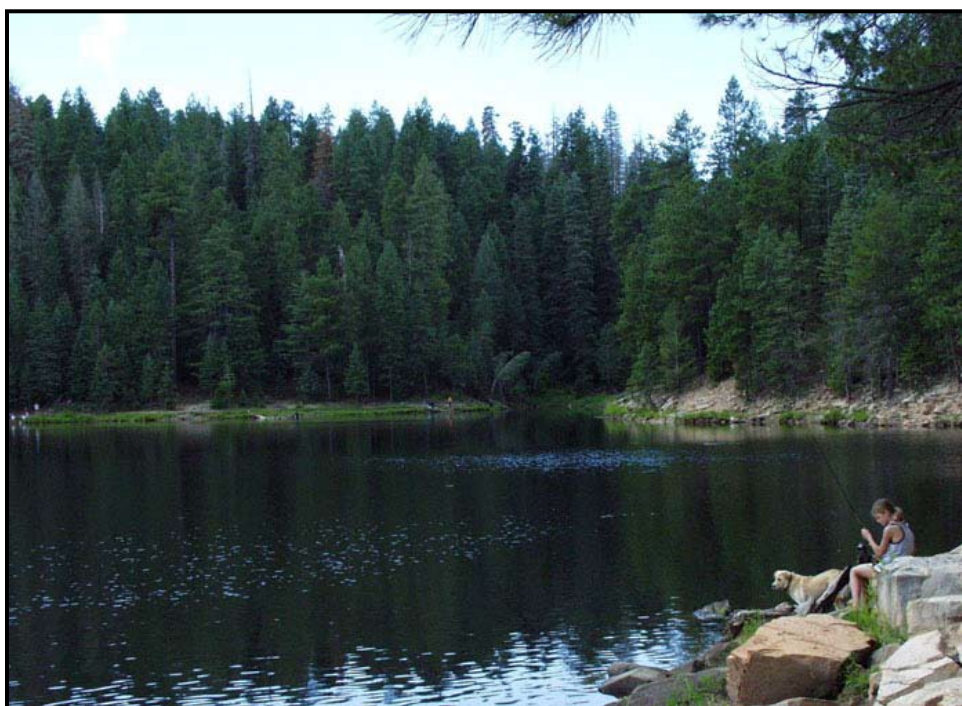


Figure 2. Steep shoreline at Bear Canyon Lake (AGFD web site)  
[http://www.azgfd.gov/h\\_f/documents/LakeGeneralDescriptionFoyer.pdf](http://www.azgfd.gov/h_f/documents/LakeGeneralDescriptionFoyer.pdf)

The surface geology along the Rim is Kaibab limestone of Permian age (formed 240 million years ago), an ancient lakebed at the edge of the Colorado Plateau which was exposed with the uplift of the Plateau. Despite a surface geology of calcium carbonate, these reservoirs have very low total alkalinity, in a range of 5.5 – 30 mg/L as bicarbonate. Rim lakes are of low to moderate productivity and are considered by AGFD to be healthy trout fisheries (Kevin Bright, personal communication).

Rim reservoir watersheds are heavily forested with Ponderosa Pine, Douglas fir, Gambel Oak and stands of Aspen. As a result, these reservoirs reflect the combined influence of snowmelt, pine litter and enhanced dissolved carbon inputs. The Ponderosa Pine forest in Northern Arizona is the largest in the United States. Historically, much of the gentle plateau country north of the Rim has been heavily logged. Today, the Rim country is managed by two national forests: the Coconino and Apache-Sitgreaves National Forests.

A paleoecological study at nearby Potato Lake (7300 ft.) indicates that dramatic changes have occurred in the area's biota over the last 35,000 years. From 35,000 to 21,000 years ago, most of the Rim was covered by a mixed conifer forest, evidence of a climate cooler and wetter than that seen today. From 21,000 to 10,400 years ago, a subalpine conifer forest dominated by Englemann Spruce was present, indicating even colder conditions. It appears that Potato lake almost dried up completely about 5000 years ago, and by 3000 years ago the forest evolved into a community much like it is today (Anderson, 1993).

### SECTION III: COMPARISON OF SIMILAR RESERVOIRS

#### ***Descriptions***

ADEQ has sampled most of the reservoirs along the Mogollon Rim. Table 1 shows basic information on the lakes in the study area.

Table 1. Description of Rim Lakes

Lake Name	Mean Basin Elev. (ft.)	Size (acres)	Watershed Size (acres)	Ratio W:L	Max/Mean Depth (ft.)	Mean Precip. (in)	Amenities	Fishery
Bear Canyon 1964	7760	60	1241.6	20.7	50/30	38.1	Picnicking, trails, toilets	Rainbow Trout and Fathead Minnow
Willow Springs 1967	7580	158	2604.8	16.5	60/30	39.8	Picnicking, boat ramps, toilets	Rainbow Trout, Tiger Trout, Largemouth and Smallmouth Bass, Green Sunfish
Knoll 1963	7610	75	2918.4	38.9	50/30	36.5	Picnicking, camping, toilets, boat ramp	Rainbow Trout, Bluehead Suckers, Fathead Minnow, Speckled Dace
Woods Canyon 1956	7670	55	5644.8	102.6	40/25	38.7	Picnicking, camping, store, boat rentals, ramp, trails, toilets	Rainbow Trout, Tiger Trout, Green Sunfish, Fathead Minnow, Golden Shiner

#### ***Initial Water Quality Data***

ADEQ began sampling Bear Canyon Lake under the Ambient Lake Program. The lake was sampled three times in 2001, in addition to once in 2000. ADEQ collected depth profile data using an YSI multiprobe and samples for lab analysis of nutrients, chlorophyll, algae identification, metals, and other inorganic parameters. The 2004 305(b) water quality assessment found the lake "inconclusive" for four out of five exceedances of low

pH, based on the Impaired Waters Identification Rule (R18-11-602) binomial method requiring 10 samples. However, EPA over-filed to add Bear Canyon to the 2004 303(d) list. As part of the Little Colorado watershed monitoring rotation, Bear Canyon was again sampled by ADEQ once in 2009 and twice in 2010. Profile data from Bear Canyon, Woods Canyon, and Willow Springs Reservoir up to 2010 each show a consistent pattern of depressed pH in a range of 5.5 – 6.5 in the lower third of the water column under stratified summer conditions (Appendix B).

### ***Trends in Water Quality with Season (2000-2010)***

Table 2 compares key water quality parameters for the four Rim lakes included in this evaluation.

Table 2. Comparison of Key Water Quality Parameters

Reservoir (# events)	Temp (°C)	DO (mg/L)	pH (SU)	Total Alk as CaCO <sub>3</sub> (mg/L)	Bicarbonate (mg/L)	SpC ( $\mu$ mhos/ cm)	Chlor-a ( $\mu$ g/L)
Bear Canyon (8)	6-21	0.42- 8.1	5.6- 8.1	5-10	5-10	18-33	< 3
Woods Canyon (19)	5-22	0.04- 9.2	5.7- 8.1	5-17	11-17	21-54	< 3 except one 15.8
Knoll (3)	9-21	1.9-8.4	6.9- 8.7	6-8	6-8	17-19	< 3
Willow Springs (10)	7-22	0.19- 7.38	5.91- 7.7	8-15	8-15	21-71	< 3

Comparison of profile data from Bear Canyon, Woods Canyon, and Willow Springs lakes shows similar patterns in both summer stratified conditions and under mixed conditions (Appendix A).

A summary of key points includes:

- Alkalinity is low in a range of 5 to 17 mg/L as bicarbonate
- All lakes may ice over (all or part); as a result mixing occurs in fall and spring
- All lakes stratify strongly in mid to late summer; temperature gradient and DO gradient are steep
- During stratified period, DO loss in the hypolimnion (below the thermocline) may reach hypoxic (3 mg/L) to anoxic (< 1 mg/L) levels
- Depending on lake depth and degree of stratification, low pH (< 6.5 SU) is present in the bottom 1-6 meters (10-40 percent of water column)
- Productivity in lakes with smaller watershed to lake area ratios is low to moderate (chlorophyll-a under 4  $\mu$ g/L), whereas lakes with a larger watershed to lake area ratio show higher productivity (chlorophyll-a >10  $\mu$ g/L)
- Periods of lower pH and DO are accompanied by negative ORP, indicating moderately to strongly reducing conditions
- Earlier sampling did not show exceedances of metals, but because of low alkalinity and hardness, typical detection limits are not low enough to confirm that there are no issues with metals mobilization
- Wet years, with high snowpack and snowmelt, allow these lakes to flush; pH, DO, and ORP levels are moderated in the following stratification period



## SECTION IV: DISCUSSION OF pH-RELATED PHENOMENA

### **pH**

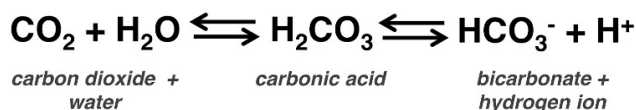
One of the most common analyses in soil and water testing is pH, the standard measure of how acidic or alkaline a solution is. It is measured on a scale from 0 – 14 Standard Units (SU). A pH of 7 is neutral; a pH less than 7 is acidic; a pH greater than 7 is basic. The closer pH gets to 1, the more acidic is the waterbody. The closer pH gets to 14, the more basic (or alkaline) is the waterbody. The pH scale is logarithmic, which means that a unit *decrease* in pH equals a ten-fold *increase* in acidity. Hydrogen (H<sup>+</sup>) ions control acidity levels. pH measures the concentration of H<sup>+</sup> and hydroxide (OH<sup>-</sup>) ions which make up water (H<sub>2</sub>O: H<sup>+</sup> + OH<sup>-</sup>), such that  $\text{pH} = -\log_{10}(\text{H}^+)$ . When the two ions are in equal concentration, the water is neutral, whereas the water is acidic if  $\text{H}^+ > \text{OH}^-$  and basic when  $\text{OH}^- > \text{H}^+$ . Most surface water in Arizona is alkaline, in the range from 7.0 to 9.0 SU. Some factors that influence pH in lakes include:

- Surface geology and soils, e.g., limestone (higher pH) vs granite (lower pH)
- Soil chemistry/leaching of soil nutrients
- Vegetation (organic decomposition byproducts)
- Acid rain (e.g., burning of fossil fuels that emit sulfur dioxide or nitrous oxides lowers pH)
- Fluctuations in carbon dioxide levels (CO<sub>2</sub>).. partial pressure (N deposition)
- Degree of productivity

Most aquatic organisms prefer a pH in the range of 6.5-8.5 SU. Unpolluted rain has a pH that is slightly acidic at 5.6 SU. EPA considers lakes with a pH less than 5 SU to be “acidified”. From the 1986 Quality Criteria for Water (EIFAC 1969; Alabaster and Lloyd, 1980): “Low pH can cause release of toxic elements or compounds under reducing conditions where oxygen is lacking.” The lower pH values in Bear Canyon Lake are in the range of 5.5-6.5 SU, a range similar to black coffee and uric acid. The most likely sources of lower pH in the Mogollon Rim area are the following (from Cook, web site):

- Direct inputs of carbon dioxide (CO<sub>2</sub>) in rain and snow; CO<sub>2</sub> dissolved in water forms a mild acid,
- Unpolluted rain water has a pH of 5.6,
- CO<sub>2</sub> levels increase during plant and algal respiration at night, resulting in lower pH values,
- Dissolution of CO<sub>2</sub> from root respiration and microbial decomposition (in watershed and lake sediments),
- Ammonium and other cation uptake by roots,
- Nitrification (The oxidation of an ammonia compound into nitric acid, nitrous acid, or any nitrate or nitrite, especially by the action of bacteria), and
- Oxidation of sulfur and nitrogen-containing organic matter.

The kinetics of CO<sub>2</sub> dissociation in lake water is crucial to understanding the tendency toward low pH in Rim lakes under summer stratified conditions when the temperature and density barriers established around the lake thermocline effectively cut off exchange between the upper and lower layers. Microbial decomposition uses up oxygen and produces CO<sub>2</sub>. Aqueous CO<sub>2</sub> dissociates to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>), which in a closed hypolimnetic system, results in lowered pH (addition of H<sup>+</sup>) and bicarbonate:



### **Alkalinity**

Alkalinity is the buffering capacity of a water body. It measures the ability of water bodies to neutralize acids and bases, thereby maintaining a fairly stable pH. Water that is a good buffer contains compounds such as bicarbonates, carbonates, and hydroxides, which combine with H<sup>+</sup> ions from the water thereby raising the pH (more basic). Total alkalinity is used as an index of sensitivity because it expresses the acid-neutralizing capacity of water bodies and thus their relative sensitivity or tolerance to acid inputs. Alkalinity comes from rocks and soils, salts, and certain plant activities. Mountain lakes fed directly by snowmelt have very low alkalinity, since the water feeding them doesn't have much time to interact with the geology. Bear Canyon Lake alkalinity is very low, in a range between 5-15 mg/L.

### **Organic Acids**

Dissolved organic matter, measured as dissolved organic carbon (DOC), is an important component of aquatic ecosystems and of the global carbon cycle. Dissolved carbon is oxidized by microorganisms to allow uptake of carbon by algae and plants. At the sediment interface and in the lower water column under low oxygen conditions, dissolved carbon is reduced by microorganisms that liberate CO<sub>2</sub> which dissociates to carbonic acid below pH of 6.4, or bicarbonate between pH of 6.4 and 8.3 SU. The dominant carbon form at Bear Canyon Lake is bicarbonate, despite the limestone surface geology. At pH above 8.3 SU in aqueous systems, most carbon is found in the carbonate form and corresponds to high alkalinity, which is commonly the case in most Arizona reservoirs.

Much of Arizona is characterized by aridisols, soils of dry climates, and entisols, young soils. The Mogollon Rim region, exhibiting extensive pine forests, is dominated by alfisols, mildly acidic clays often associated with pine forests. (From U.S. Department of Agriculture, Natural Resources Conservation Service, University of Idaho web site).

Surface runoff can transport significant loads of nutrients and organic matter from a catchment to a lake, especially when the surrounding slopes are steep. Klimaszyk and Rzymiski (2013) found that coniferous litter has a higher impact on the level of DOC than deciduous litter. Significant DOC and ammonium peaks were observed in runoff from a Scots Pine forest in Poland, collected after heavy rainfall and during intensive snowmelt; DOC concentrations were comparable to those found in transitional and raised bogs. The resulting dystrophication (added color from humic acids) significantly affects the thermal structure, favors production by very small planktonic algae and bacteria, and may also significantly decrease pH. Runoff from birch forests, on the other hand, showed higher levels of total nitrogen and total phosphorus.

### **Variation in Snowpack**

Snow depth and the volume of water contained in snowpack vary significantly between years in Arizona. The SNOTEL station on Promontory Butte along the Mogollon Rim has recorded snow water equivalents (SWE) from 1981 to the present during snowmelt months (January – April) (NRCS web site). Records show that SWEs over this 4-month

period ranged from a low of 2.3 inches in 2006 to a high of 80.1 inches in 1985. The highest SWE recorded during a lake monitoring year was 75 inches in the spring of 2010. That summer, even when stratified, both Bear Canyon Lake and Willow Springs Lake pH readings were above 7.3 SU, even close to the bottom of the water column. Dissolved oxygen was also higher than average in the hypolimnion, reflecting the fact that both experienced significant flushing. The median SWE for the period of record is 27.6 inches.

### ***Dissolved Oxygen (DO)***

DO is a measure of the amount of oxygen dissolved in the water. In lakes, natural sources of dissolved oxygen are derived from the photosynthetic process of aquatic plants or from the atmosphere by wind turbulence or crashing waves on the water's surface (Horne and Goldman, 1994). In order to obtain a healthy fish habitat certain levels of DO need to be maintained. The numeric water quality standard in Arizona for dissolved oxygen in surface water from a single sample minimum with an A&Wc designated use is 7.0 mg/L within the first meter of the water column (A.A.C., R18-11-109, 2009). Decomposition, or the breakdown of organic matter (algae and plants) consumes DO, increases CO<sub>2</sub> and lowers pH in the lower layers of a stratified lake.

## **SECTION V. SAMPLING to FILL DATA GAPS**

In order to support a finding of “natural condition” for low pH, ADEQ collected additional samples in August 2013, June 2014, and September 2014 at Bear Canyon Lake, Woods Canyon Lake and Willow Springs Lake. The latter two sample events included low-level detection analysis for potentially toxic metals. Using Clean Hands/Dirty Hands sampling technique (Method 1669), samples were collected from the hypolimnion of each lake about one meter above the sediment. ADEQ obtained certified clean Teflon tubing, prepared with a one-meter silicon tube attached, from Brooks Rand Lab in Seattle, WA. The samples were collected by pumping lake water from depth to the surface using a Geopump. ADEQ focused Clean Hands/Dirty Hands low-level metals sampling in early and late summer of 2014, with two additional field-measurement only events sandwiched in between, as seen in Table 3.

Table 3. Study Lakes Sampling Schedule 2013-2014

Lake/Site	Date	Depths	Parameters Collected
Bear Canyon, Woods Canyon Site A (deepest)	Aug 21 & 22, 2013	Epilimnion Hypolimnion	Field profile (YSI) + secchi depth, total and dissolved metals, nutrients, inorganic chemistry, chlorophyll, algae ID, Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), sediment nutrients & metals
Bear Canyon, Woods Canyon, Willow Springs (Site A deepest)	Jun 24 & 25, 2014 Sep 23 & 24, 2014	Epilimnion Hypolimnion	Field profile (YSI) + secchi depth, total and dissolved metals, nutrients, inorganic chemistry, chlorophyll, algae ID, TOC/DOC, sediment nutrients & metals Low-level metals (Hg, Pb, Cd, Cu, Se, Zn) in water
Bear Canyon, Woods Canyon, Willow Springs (Site A deepest)	Apr 29 & May 1, 2014 Jul 29/30, 2014	1 meter increments	Field profile (YSI) and Secchi depth

Samples for dissolved metals were field-filtered using certified clean filters and preserved appropriately for shipment to the lab within 24 hours. One of three outcomes was expected: 1) all metals results are below respective criteria and sufficient refuge exists for aquatic life, 2) one or more metals results are above respective criteria, or 3) metals results

are all below respective criteria but other results indicate an insufficient “refuge” for aquatic life. In the case that results came back in support of the first outcome, ADEQ would recommend delisting low pH in reservoirs where it is determined that natural conditions alone are the cause and where the designated uses are being protected:

ADEQ in accordance with Arizona Administrative Code R18-11-605(E).2.a “shall remove a pollutant from a surface water or segment from the 303(d) List based on one or more of the following criteria”, which include Arizona Administrative code R18-11-605(E).2.a.ii and R18-11-605(E).2.a.vi, respectively:

*“The data used for previously listing the surface water or segment under R18-11-605(D) is superseded by more recent credible and scientifically defensible data meeting the requirements of R18-11-602, showing that the surface water or segment meets the applicable numeric or narrative surface water quality standard. When evaluating data to remove a pollutant from the 303(d) List, the monitoring entity shall collect the more recent data under similar hydrologic or climatic conditions as occurred when the samples were taken that indicated impairment, if those conditions still exist.”*

*“Pollutant loadings from naturally occurring conditions alone are sufficient to cause a violation of applicable water quality standards.”*

## **SECTION VI: 2013-2014 SAMPLING RESULTS**

### ***Profile Data***

Lake conditions observed by month in 2013 and 2014 were similar to previous sampling periods. Profile data can be found in Appendix A. Secchi depth was maintained consistently around four meters. Trends observed in the profile data include the following:

#### **EARLY MAY 2014:**

- water column well aerated
- no thermocline
- surface temperature 9-11 degrees C
- no low pH values
- fish refuge 100%

#### **LATE JUNE 2014:**

- thermocline steep (greater than 1 degree change per meter); metalimnion large (3-5 meters thick)
- surface temperature 17-20 degrees C
- DO drops below 3 mg/L in bottom third of water column; strongly reducing conditions
- low pH in bottom one third of water column
- fish refuge limited

#### **LATE JULY 2014:**

- thermocline steep; metalimnion large
- surface temperature 21-22 degrees C
- DO drops below 3 mg/L in bottom half of water column; entire water column reducing conditions except in Willow Creek
- Low pH in bottom half of water column

- fish refuge further limited

**LATE AUGUST 2013:**

- thermocline steep; metalimnion moderate
- surface temperature 21 degrees
- DO drops below 3 mg/L in bottom half of water column; strongly reducing in bottom half of water column at Bear Canyon and bottom third at Woods Canyon
- low pH following reducing trend
- fish refuge limited

**LATE SEPTEMBER 2014:**

- thermocline less steep; metalimnion moderate
- surface temperature 19-20 degrees C
- DO drops to below 3 mg/L in bottom third of water column; entire water column reducing conditions
- low pH in bottom third of water column
- fish refuge limited but improving

**Low Level Metal Analysis**

The results of the low level metals analyses in the summer of 2014, with the addition of iron, can be seen in Table 4 as compared to their most conservative water quality standard (WQS). Cadmium (Cd), Copper (Cu), Lead (Pb), Zinc (Zn) and Mercury (Hg) results did not exceed standards.

Table 4. Hardness-based Dissolved Metals; Dissolved Fe, Hg and Total Se

Reservoir (# events)	Depth (m)	Redox (mv)	DO (mg/L)	pH	Hardness (mg/L)	D Cd (ug/L)	D Cu (ug/L)	D Pb (ug/L)	D Zn (ug/L)	D Hg (ng/L)	D Fe (ug/L)	T Se (ug/L)
<b>WQS</b>					<b>@25</b>	<b>0.09</b>	<b>2.74</b>	<b>0.54</b>	<b>36.2</b>	<b>10</b>	<b>1000</b>	<b>2</b>
<b>Bear Canyon</b> 6/25/2014 9/24/2014	11.5 12	-130 -335	3.08 0.68	5.94 6.27	<33 <33	<0.007 <0.007	0.565 0.450	0.182 0.362	0.48 0.30	3.99 7.36	1,710 2,560	0.211 0.166
<b>Woods Canyon</b> 6/25/2014 9/24/2014	9 9	-212 -285	0.96 0.44	5.62 6.23	<33 <33	<0.007 <0.007	0.475 0.284	0.505 0.490	0.58 0.93	4.86 8.36	2,670 4,890	0.119 0.109
<b>Willow Springs</b> 6/24/2014 9/23/2014	14 14	-143.8 -224	0.77 0.75	5.86 6.51	<33 <33	<0.007 <0.007	0.673 0.569	0.008 0.178	0.32 0.41	1.09 0.96	<200 709	0.133 0.134

Blue=hardness dependent

Only dissolved Fe (iron) at Bear Canyon and Woods Canyon was greater than the associated dissolved standard of 1000 ug/L. These two lakes have steep forested watersheds with naturally iron-rich soils. Dissolved iron at Woods Canyon was greater than at Bear Canyon Lake, in keeping with its larger watershed to lake size. Previous samples collected for total iron show the same trend of higher iron in deep samples during stratification (Appendix B), but Arizona does not have a standard for total iron.



### General Chemistry by Lake

Willow Springs Lake is partially spring fed and has a smaller watershed-to-lake ratio than Bear Canyon Lake. Apparently, conditions in this lake do not promote high dissolved iron concentrations. Summarizing the major ion signature, Table 5 shows that sodium, chloride and specific conductivity are significantly higher at Willow Springs Lake, which may provide partial buffering to potentially toxic iron complexes.

Table 5. General Chemistry by Lake (Summer of 2014)

Reservoir	pH (SU)	Total Alkalinity (mg/L)	Bi-carbonate (mg/L)	Chloride (Cl <sup>2-</sup> ) (mg/L)	Sodium (Na <sup>2-</sup> ) (mg/L)	Sulfate (SO <sub>4</sub> <sup>2-</sup> ) (mg/L)	TSS (mg/L)	Specific Conductivity (umhos/cm)
<b>Bear Canyon</b> 6/25/2014 9/24/2014	5.99-7.99 5.88-7.20	6.2-8.9 6.2-11.7	6.2-8.9 6.2-11.7	0.91-1.0 0.96-0.98	0.830 0.845	1.5-1.8 0.85-1.6	<5-11 <5	10.9-12.7 19.5-24.6
<b>Woods Canyon</b> 6/25/2014 9/24/2014	5.62-6.55 6.17-7.87	12.4-14.4 12.4-16.2	12.4-14.4 12.4-16.2	0.86-0.87 0.90-1.0	0.836 0.870	<0.5-0.93 0.55-0.73	<5-12 <5	14.0-22.4 26.0-30.2
<b>Willow Springs</b> 6/24/2014 9/23/2014	5.86-7.25 6.33-8.57	9.7-9.9 9.5-10.8	9.7-9.9 9.5-10.8	9.6-10.3 9.6-10.1	6.27 6.29	1.6-1.8 1.6-1.8	<5 <5	36.8-72.1 76.0-131.0

This very low conductivity corresponds to low Total Dissolved Solids (TDS) values, suggesting that iron may not be present as iron salts. In addition, both Bear Canyon and Woods Canyon showed higher suspended solids that did not correspond to low secchi or high chlorophyll. It may be that colloiddally-bound iron from blowing dust or mobilized by spring snowmelt/runoff is contributing to suspended solids.

### Discussion of Iron Results

Mentioned previously, microbial decomposition in the hypolimnion uses up oxygen and produces CO<sub>2</sub>. Aqueous CO<sub>2</sub> dissociates to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>), which in a closed hypolimnetic system acts like a nonvolatile diprotic acid (H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>), so that the proton conditions for the closed system are H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>:

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \text{ or approximately,} \\ [H^+] = [HCO_3^-] \text{ (bicarbonate)}$$

The consumption of oxygen, formation of carbonic acid, and consequent decrease in pH promote formation of ferrous iron and dissolved forms of organic carbon and colloidal material. Knowledge of the pH condition of the environment is not sufficient for predicting the form in which an element will exist in natural waters. One must also take into consideration whether the aqueous environment is well-aerated (oxidizing) or affected by organic wastes (reducing). Creation of a 'predominance diagram' includes the reduction potential of the environment as well as the pH. This type of predominance diagram is known as a Pourbaix diagram, E<sup>o</sup>-pH diagram, or pE-pH diagram (Figure 3) (reprinted from Nordstrom and Munoz, 1985, [www.wou.edu/las/physci/ch412/pourbaix.htm](http://www.wou.edu/las/physci/ch412/pourbaix.htm)).

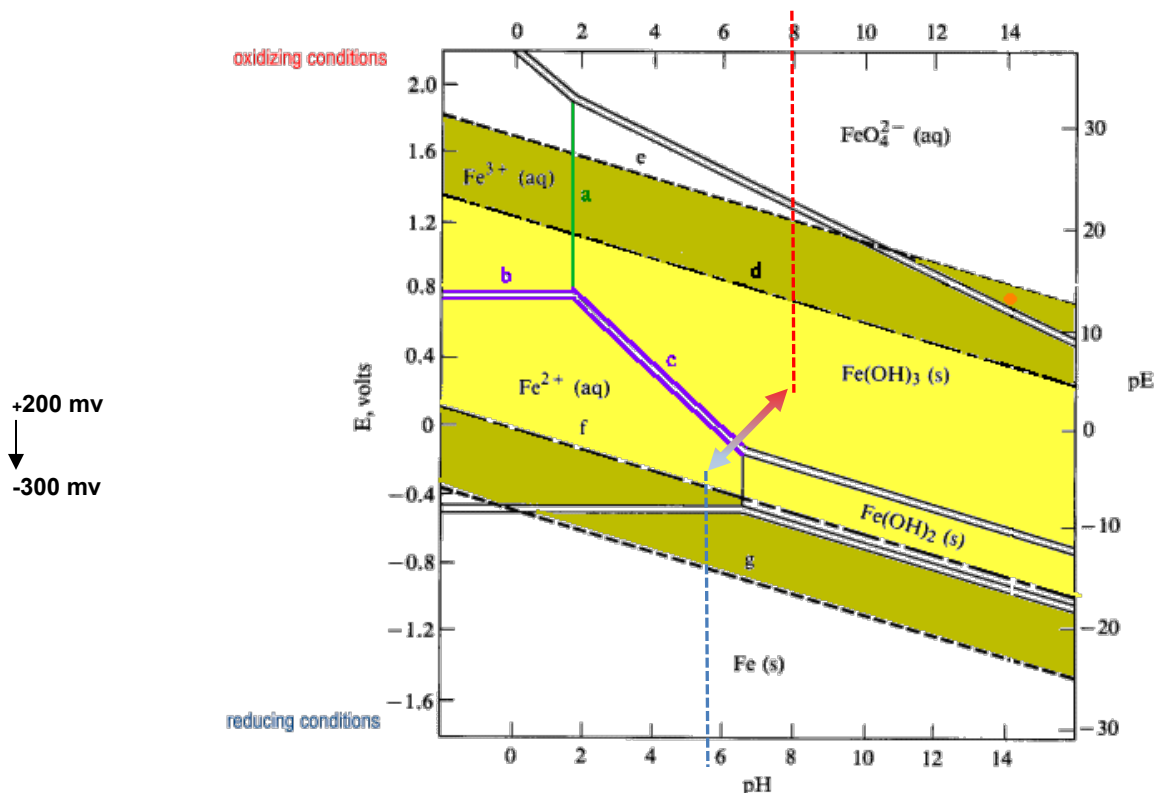


Figure 3. Simplified Pourbaix diagram for 1 molar (M) iron solutions at 25 degrees C (blue to red line depicts conditions in Bear Canyon and Woods Canyon lakes)

Based on the redox measurements obtained (+200 down to -300 mv), the blue and red arrow in Figure 4 shows that the default dominant iron species in these lakes would be a form of iron hydroxide,  $\text{Fe(OH)}_3$  as the oxidized “ferric” form and  $\text{Fe(OH)}_2$  as the reduced “ferrous” form. Early data from Hutchinson and others (1938) showing differences at depth in lakes show dissolved iron, presumably in the ferrous ( $\text{Fe}^{++}$ ) state increases and Eh decreases as the dissolved oxygen decreases. Water trapped below the thermocline will contain increasing amounts of ferrous or reduced iron as oxygen is depleted, which according to Hem et. al (1962) can reach solutions as high as 5000 ug/L.

Iron speciation is highly affected by the chemical composition of the lake water, iron inputs and removal processes, as well as internal recycling. The physicochemical speciation of iron, which profoundly influences its bioavailability, depends on the relative importance of various competing processes including adsorption-desorption, precipitation-dissolution, ion exchange, complexation-dissociation, and redox reactions. According to Xing and Liu (2011), a method based on size separation has been accepted and applied in limnology: operationally defined filtration and ultra-filtration techniques set boundaries in the continuum between dissolved, colloidal and particulate phases. Accordingly, iron in lake water is separated for three size fractions: particulate iron ( $>0.22 \mu\text{m}$ ), colloidal iron ( $0.025\text{--}0.22 \mu\text{m}$ ) and soluble iron ( $<0.025 \mu\text{m}$ ). The highly reactive colloidal iron may either coagulate or flocculate to form larger particles, or become soluble. In addition to controlling iron solubility, the formation of colloidal and larger, more refractory iron particles provides a mechanism for removing dissolved iron and other trace metals from the water by adsorption and co-precipitation.

Iron is a key nutrient, important in various aspects of cell and organism function. Xing and Liu found that size-fractionated iron could transform into each other, especially the highly reactive colloidal iron. Most freshwater phytoplankton, especially cyanobacteria, can secrete organic  $\text{Fe}^{3+}$ /metal-chelating molecules that serve to solubilize and scavenge the ferric from of iron from the environment; some cyanobacteria have the ability for luxury consumption of iron. These colloidal iron complexes as well as iron in phytoplankton will be part of the dissolved fraction measured with use of a 45  $\mu\text{m}$  filter, in addition to some of the particulate-bound iron.

Studies of acid bog lakes (Koenings, 1976) and other soft water lakes where organic acids (humic material) are prevalent (Collienne, 1983) have shown that colloidal reactive ferric iron predominates the oxygenated epilimnion. As colloidal ferric iron moves to deeper layers, some remains reactive and some becomes dissolved ferrous iron. Ferrous iron can be maintained in partially oxygenated water by photoreduction of complexed reactive  $\text{Fe}^3$  with an associated drop in redox potential. In this type of system, the inorganic form of iron hydroxide is present only in minor quantities; this condition may also promote greater retention of phosphate that would otherwise precipitate, available for uptake by phytoplankton.

Humic material from pine litter provides a more likely platform for complex with ferric or ferrous iron in mildly acidic unstable conditions than complexes with cations such as chloride or sulfate. Ffolliott estimated that annual needle drop in a typical Arizona ponderosa pine forest is between 1000 and 2000 lbs/acre (unpublished Forest Service research, cited in Seawell et. al, 1969). When covered in snow, the litter is soaked by melt water; leachate of these materials moves into impoundments in runoff when accelerated snow melt occurs. Considering the average water content of snow (approximately 8 inches), there are from 0.5 to 1.0 grams of new needle litter per liter of snow melt. (Barr, 1956).

In Bear Canyon, Woods Canyon, and Willow Springs lakes, organic carbon was measured in a range of 6.5 – 8.5 mg/L. Dissolved organic carbon was found to decrease in the hypolimnion, reduced by microorganisms that liberate  $\text{CO}_2$  which dissociates to carbonic acid below pH of 6.4. Total and dissolved organic carbon results in the summer of 2014 can be seen in Table 6.

Table 6. Organic Carbon by Lake (Summer 2014)

Reservoir	TOC (mg/L)	DOC (mg/L)	TOC (mg/L)	DOC (mg/L)
	Deep		Shallow	
<b>Bear Canyon</b> 6/25/2014 9/24/2014	7.7 @ 11.5m 7.4 @ 12m	5.8 @ 11.5m 4.4 @ 12m	7.6 @ 2.7m 6.5 @ 3.2m	5.9 @ 2.7m 4.0 @ 3.2m
<b>Woods Canyon</b> 6/25/2014 9/24/2014	8.5 @ 9m 8.2 @ 9m	6.3 @ 9m 4.2 @ 9m	10.1 @ 2.3m 7.9 @ 3.1m	8.0 @ 2.3m 5.8 @ 3.1m
<b>Willow Springs</b> 6/24/2014 9/23/2014	7.0 @ 14m 6.3 @ 14m	5.2 @ 14m 3.1 @ 14m	NA 6.8 @ 3m	NA 5.0 @ 3m

### ***Iron Toxicity and Iron Criteria***

Depending on the form of iron present, it may be toxic to fishes. Vuorinen et al, 1998, found that aluminum and iron, in concentrations found in the natural environment, may be toxic both to brown trout and grayling, and the toxicity of these metals is augmented with

increasing acidity. Even though these species are no longer found in Bear Canyon Lake, it is not yet known if dissolved iron is affecting existing species. Even in slightly acidic water, the increase in the concentrations of these metals will make the water more harmful to fish. Dissolved humic substances reduce the toxicity of iron and/or aluminum but do not entirely prevent it. (Vuorinen et al, 1998). Peuranen et al. (1994) observed damage in the gills of one-summer-old brown trout exposed to Fe(II) and Fe(III) at pH 5 and 6.

There are no EPA established national 304(a) acute or chronic criteria for iron, and toxicity studies of iron on aquatic life are rare. Most states have adopted the EPA (Red Book) recommended iron criterion of 1 mg/l (total iron) as the chronic criterion even though EPA did not identify whether it was meant to apply to acute or chronic toxicity.

The Iowa DNR (web site) has adopted the total iron EPA criteria as an acute criterion for ease of use in discharge permits. They reason that even though dissolved iron is bioavailable and more toxic to aquatic life, particulate iron, when suspended in water, may be detrimental to fishes and other aquatic life. Particulate iron can settle to form flocculants, materials that cover stream bottoms thereby destroying bottom-dwelling invertebrates, plants, or incubating fish eggs. Iowa allows for departure from this criterion if a valid site specific acute whole effluent toxicity test demonstrates that the LC0 or the "Non-Observed-Adverse-Effect Concentration" (NOAEC) for iron is higher than 1 mg/L.

Under Indiana rules, calculation based on the Percent Inhibitory Concentration (ICp) for warm water iron criteria resulted in much higher acute and chronic values: 5.5 mg/L final acute value (FAV), 2.7 mg/L acute (AAC) and 2.5 mg/L chronic (CAC) (Indiana web site).

A more restrictive criteria has been proposed by the Province of British Columbia (2008) for chronic iron exposure. Based on the lowest 96-hr LC<sub>50</sub> for the amphipod *Hyalella* of 3.6 mg/L, and supported by the LC<sub>50</sub> value of 3.5 mg/L for the green alga *Selenastrum*, they proposed to divide by a safety factor of 10 and arrived at a chronic criteria value of 0.35 mg/L or 350 µg/L.

Arizona's criteria of 1 mg/L for dissolved iron is applied as a chronic standard. The dissolved iron results obtained from Bear Canyon Lake and Woods Canyon Lake are relatively high, however what forms the iron is in and the degree of bioavailability cannot be proven. Although there are salmonids present, these lakes are really cool water fisheries (AGFD, personal communication) and most fish overwinter. There is likely some degree of chronic toxicity at Bear Canyon and Woods Canyon lakes. Despite this, there have been no reported fish kills at either lake.

## SECTION VII: SUMMARY AND RECOMENDATIONS

The lakes evaluated in this report were all constructed explicitly for recreation. The primary recreational uses of these reservoirs is fishing, picnicking, and camping. In Arizona, the AGFD has three trout hatcheries and stocks the Rim lakes with Rainbow trout in the spring and fall. Based on amenities and access, Woods Canyon Lake is the most visited/fished lake along the Mogollon Rim. According to Kevin Bright from AGFD (personal communication):

*Woods Canyon Lake is managed as a put and take fishery. We can hardly put enough fish in there to keep up with angler pressure. The trout that we put in there seem to do very well. We do not see water quality issues or fish survival issues. I*

*believe that some trout will be resident past the stocking season, over winter and show good growth the following spring.*

*Woods Canyon Lake and Bear Canyon Lake do not have high nutrient productivity. They have low calcium and magnesium concentration and very low alkalinity (all values  $\leq$  to 15) from our data. Conductivity seems to average in the high 20 umhos/cm range. Therefore these lakes are poorly buffered and susceptible to pH variability. We suspect that low pH at these lakes is from dissolved organics from pine needles, low productivity, and poorly buffered water chemistry. We also would suspect some atmospheric deposition from Phoenix contributing to low pH.*

The acceptable range of pH to aquatic life, particularly fish, depends on numerous other factors, including prior pH acclimatization, water temperature, dissolved oxygen concentration, and the concentrations and ratios of various cations and anions (McKee and Wolf, 1963, cited in Roberson-Bryan, Inc. May 2004). Alabaster and Lloyd (1980) identified the pH range that is not directly lethal to freshwater fish as 5.0 – 9.0. Robertson-Bryan, Inc., May 2004, provides a detailed review of studies on several species of fish, aquatic invertebrates, plants, and plankton in relation to both low and high pH. They corroborate the range of 5.0 – 9.0 for most fish and include trout in that range. In addition, the low threshold for macroinvertebrate diversity is a pH of 4.0, which is below any value of pH found at the Rim lakes.

Natural condition is a term that describes the quality of surface water that exists in the absence of human-caused pollution or disturbance. The following ADEQ rules apply in consideration of designated use criteria:

#### Arizona's R18-11-115 Site-specific Standards

- A. The Director shall adopt a site-specific standard by rule.
- B. The Director may adopt a site-specific standard based upon a request or upon the Director's initiative for any of the following reasons:
  - 1. Local physical, chemical, or hydrological conditions of a surface water such as pH, hardness, or temperature alters the biological availability or toxicity of a pollutant;
  - 2. The sensitivity of resident aquatic organisms that occur in a surface water to a pollutant differs from the sensitivity of the species used to derive the numeric water quality standards to protect aquatic life in Appendix A;
  - 3. Resident aquatic organisms that occur in a surface water represent a narrower mix of species than those in the dataset used by the Department to derive numeric water quality standards to protect aquatic life in Appendix A; or
  - 4. The natural background concentration of a pollutant is greater than the numeric water quality standard to protect aquatic life prescribed in Appendix A.
- C. Site-specific study..(1-4)
  - ..4. Natural background
    - ..b. The Director may establish a site-specific standard at a concentration equal to the natural background concentration.

Evaluation of the data used for the 2004 water quality assessment and subsequent data collected since that time, demonstrate what appears to be a naturally occurring condition:



low alkalinity waters under prolonged periods of steep thermal and chemical stratification, results in pH below the lower bound of the pH standard, in a range from 5.6 to 6.5 between 10 and 13 meters deep. pH has not been found below 5.6. Based on 2013 and 2014 data, the 2016 assessment says AgL, FBC and A&W uses are attaining, since low pH is considered to be due to natural conditions in these deep narrow lakes.

Prior to 2013, due to high lab detection limits, it had not been possible to assess attainment of some dissolved metals criteria, specifically, Cd, Cu, Cr, Zn and Pb which are pH and hardness dependent. In addition, the A&W criteria for dissolved mercury (Hg) and total selenium (Se) were also below standard detection limits.

With the 2014 low level analyses, data show that pH between 5.6 and 6.5 SU in the hypolimnion of Bear Canyon and Woods Canyon lakes did not result in exceedances of hardness-related metals, mercury or selenium. However, dissolved iron was relatively high in the hypolimnion in two summer sampling events and may be an issue. Fish are not likely to come into contact with high iron associated with bottom waters that lack oxygen since they would naturally avoid those layers (M. Dahlberg, AGFD, personal communication). ADEQ will collaborate with AGFD to collect a cross-section of resident fish species from these lakes in order to assess potential toxicity from iron that might be associated with fall turnover. Hatchery fish will be compared to lake resident fish. ADEQ will collect additional total and dissolved iron water samples and total iron in sediment of both lakes prior to the fish assessment. If evidence is found that fish are negatively affected by iron, remediation may be pursued.

As there are no mines, point sources or anthropogenic activities within the three watersheds, ADEQ proposes that low pH (5.6-6.5 SU) is a natural condition of these lakes. There appears to be grounds for development of site-specific pH expectations in these lakes.

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***GLOSSARY of LIMNOLOGICAL TERMS***

Productivity	rate of biomass production (algae and plants)
Decomposition	breakdown of biological material mitigated by microorganisms
Biomass	plant and animal material
Stratification	condition of a lake when a thermocline is present
Thermocline	where the vertical temperature profile in a lake drops more than 1 degree per meter depth
Epilimnion	upper layer of water above thermocline; area of highest productivity
Hypolimnion	bottom layer of water below thermocline; area of highest decomposition
Chemocline	part of the lake profile where loss of oxygen results in 'reduced' forms of chemicals; this condition may promote accumulation of potentially toxic metals or organic compounds
Low pH	less than 6.5 SU



## Appendix A: 2013 and 2014 Lake Profile Data

Table A-1. Comparison of Seasonal Profiles (2013-2014)

Site	Date	Temp	Depth	ORP	DO	pH	Site	Date	Temp	Depth	ORP	DO	pH	Site	Date	Temp	Depth	ORP	DO	pH	Site	Date	Temp	Depth	ORP	DO	pH	Site	Date	Temp	Depth	ORP	DO	pH
WCL <sup>1</sup>	8/22/2013	21.55	0.1	120	6.45	8.37	WCL	5/1/2014	10.73	0.1	63	9.73	7.83	WCL	6/25/2014	20.08	0.1	95	7.55	6.57	WCL	7/30/2014	22.6	0.1	-12.9	6.37	7.65	WCL	9/24/2014	20.56	0.1	-85.2	7.51	7.87
		21.31	1	123	6.32	7.88			9.94	1	69	9.62	7.7			19.9	1	93.9	7.6	6.55			22.57	1	-21	6.22	7.59			19.38	1	-87	7.85	7.8
		21.23	2	133	6.26	7.56			9.78	2	70	9.45	7.66			19.66	2	93	7.68	6.55			22.49	2	-19.5	6.05	7.53			19.04	2	-87.5	7.85	7.75
		21.12	3	140.8	6.19	7.35			9.7	3	71	9.41	7.61			19.45	3	92	7.66	6.54			22.16	3	-18.5	6	7.49			18.88	3	-87.5	7.74	7.65
		20.59	4	149	5.5	7.14			9.64	4	74	9.39	7.55			18.13	4	96	7.73	6.46		T	20.99	4	-22	5.13	7.22			18.7	4	-84.5	6.62	7.38
	T	19.00	5	72	1.21	6.65			9.57	5	74	9.28	7.52		T	14.87	5	104.9	7.27	6.23		T	17.53	5	-42	3.32	6.8			18.35	5	-85.6	5.05	7.11
	T	16.46	6	44	0.6	6.49			9.3	6	78	8.92	7.44		T	12.77	6	107.8	4.6	6.01		T	14.3	6	-55.5	2.04	6.55		T	16.97	6	-124.5	0.88	6.78
		12.38	7	-58	0.35	6.29			8.75	7	82	8.44	7.34			8.46	7	-197	2.2	5.86			10.7	7	-55.5	2.15	6.42		T	14.67	7	-136.9	0.51	6.41
		9.56	8	-75	0.34	6.01			7.98	8	83	6.4	7.07			8.56	8	-212	1.03	5.73			8.93	8	-151	2.07	6.34			10.72	8	-153	0.47	6.3
		8.18	9	-182	0.31	5.8			7.5	9	82	5.8	7			8.17	9	-212	0.96	5.62			8.46	9	-355	1.92	6.31			9.48	9	-285	0.44	6.23
		7.85	9.5	-209	0.26	5.74			7.3	10	78	5.38	6.79										8.24	9.6	-358	1.81	6.31			8.78	10	-306	0.42	6.17
																windy																		
Site	Date	Temp	Depth	ORP	DO	pH	Site	Date	Temp	Depth	ORP	DO	pH	Site	Date	Temp	Depth	ORP	DO	pH	Site	Date	Temp	Depth	ORP	DO	pH	Site	Date	Temp	Depth	ORP	DO	pH
BCL <sup>2</sup>	8/21/2013	21.32	0.1	145	6.72	7.57	BCL	4/30/2014	9.71	0.1	112	9.39	8.54	BCL	6/25/2014	17.87	0.1	117	7.15	8.21	BCL	7/30/2014	21.84	0.1	-21.8	6.09	7.23	BCL	9/24/2014	19.1	0.1	-84.8	7.07	7.2
		21.09	1	144	6.71	7.31			9.65	1	118	9.32	8.18			17.87	1	118	7.01	7.99			21.71	1	-22.2	6.11	7.23			18.74	1	-85	7.08	7.15
		20.89	2	148	6.7	7.09			9.63	2	122	9.36	7.95			17.85	2	118.9	6.95	7.85			21.54	2	-21.6	6.08	7.21			18.59	2	-85.3	8.47	7.17
		20.73	3	132	6.66	7.01			9.61	3	129	9.19	7.48			17.83	3	118.4	6.94	7.58			21.31	3	-20.5	6.08	7.19			18.5	3	-81.8	8.41	7.13
		20.22	4	111	6.62	6.95			9.52	4	130	9.16	7.4			17.81	4	115	6.91	7.57			20.94	4	-19.2	6.03	7.13			18.29	4	-81	8.32	7.06
	T	18.43	5	92	4.86	6.64			9.47	5	130	9.21	7.35			17.76	5	110.5	6.91	7.34		T	19.16	5	-12.3	5.86	7			18.14	5	-80.5	8.11	7.01
	T	15.65	6	75	3.01	6.36			9.45	6	130	9.14	7.32		T	15.97	6	110.9	7.19	7.29		T	16.98	6	-10.3	5.74	6.9			17.93	6	-77.1	7.82	6.91
		11.78	7	-75	2.23	6.19			9.38	7	130	9.21	7.24		T	14.6	7	117.3	7.33	7.1		T	15.29	7	-8.5	5.11	6.71		T	16.78	7	-82.4	5.98	6.57
		9.95	8	-179	2.39	6.09			9.24	8	131	9.17	7.21		T	12.84	8	131.3	7.45	6.75		T	13.44	8	-7.4	4.49	6.55		T	15.3	8	-88.1	3.04	6.24
		8.77	9	-177	2.22	6.04			9.16	9	132	8.94	7.13			11.36	9	138	7.25	6.52		T	11.69	9	-12.4	3.71	6.39			12.83	9	-89.5	1.73	6.04
		8	10	-174	1.96	5.97			8.88	10	134	8.65	7.06			10.7	10	141.5	6.64	6.15			10.38	10	-53.2	2.2	6.18			10.68	10	-259	1.15	5.93
		7.4	11	-178	1.21	5.87			7.9	11	137	8.01	6.85			9.03	11	5.5	5.49	5.99			8.97	11	-329	1.71	6.25			9.87	11	-320	0.74	6.03
		6.96	12	-163	0.43	5.71			7.44	12	139	7.53	6.71			8.72	11.5	-130	3.08	5.94			8.67	12	-343	1.68	6.27			9.1	12	-335	0.68	5.88
		6.9	13	-169	0.42	5.63			7.24	13	139	6.48	6.63										8.47	13	-360	1.66	6.29							
									7.2	13.6	140	5.71	6.57				windy..max 13.6m						8.41	14	-369	1.64	6.31							
																							8.39	14.6	-394.8	1.62	6.32							
Site	Date	Temp	Depth	ORP	DO	pH	Site	Date	Temp	Depth	ORP	DO	pH	Site	Date	Temp	Depth	ORP	DO	pH	Site	Date	Temp	Depth	ORP	DO	pH	Site	Date	Temp	Depth	ORP	DO	pH
							WIS <sup>3</sup>	5/1/2014	10.2	0.1	65	10.02	8.57	WIS	6/24/2014	18.71	0.1	132	7.96	7.45	WIS	7/29/2014	22.6	0.1	50	6.52	7.96	WIS	9/23/2014	19.68	0.1	-12.8	7.69	8.57
									10.17	1	70	10.04	8.34			18.7	1	132.9	7.92	7.25			22.58	1	44.4	6.39	7.88			19.6	1	-18.5	7.62	8.27
									10.06	2	69	10.05	8.22			18.69	2	132	7.91	7.13			21.84	2	40.1	6.36	7.86			19.56	2	-22.6	7.58	8.17
									9.99	3	75	10.01	8.08			18.65	3	131.2	7.91	7.06			21.7	3	38.6	6.43	7.85			19.13	3	-27.5	7.58	8.05
									9.91	4	80	10.04	7.93			18.64	4	131	7.9	6.99			21.65	4	36.3	6.37	7.83			19.04	4	-27.2	7.56	7.99
									9.71	5	85	9.96	7.83			18.36	5	129.8	7.96	6.94			21.05	5	37.6	6.06	7.67			19.02	5	-29.9	7.5	7.94
									9.56	6	88	9.88	7.77		T	16.69	6	127	8.35	6.91			19.06	6	43.5	5.69	7.48			18.86	6	-31	7.19	7.88
									9.51	7	90	9.79	7.71		T	15.42	7	128.8	8.58	6.86		T	17	7	48.4	4.65	7.28			18.62	7	-30	6.39	7.74
									9.47	8	91	9.81	7.7		T	13.49	8	129.1	8.95	6.83		T	15.05	8	49.6	3.15	7.03			17.83	8	-34.7	3.44	7.43
									9.44	9	91	9.74	7.66			11.58	9	88	6.93	6.53			12.97	9	35.2	0.99	6.62		T	15.95	9	-52.8	1.16	7.1
									9.41	10	92	9.73	7.65			10.71	10	5.3	2.15	6.33			11.74	10	18.5	0.87	6.56			13.43	10	-65.5	0.79	6.92
									9.3	11	95	9.55	7.6			9.56	12	-87.7	0.81	5.96			10.69	11	-176.4	0.9	6.51		T	11.93	11	-73.8	0.75	6.79
									8.62	12	100	9.07	7.55			9.03	14	-143.8	0.77	5.86			10.04	12	-213	0.89	6.46			11.07	12	-140.7	0.77	6.69
									8.05	13	102	8.26	7.45			8.3	16	-179	0.6	5.83			9.53	13	-287	0.87	6.43			10.37	13	-202	0.76	6.6
									7.85	14	104	7.81	7.4										9.13	14	-335	0.92	6.4			9.87	14	-224	0.75	6.51
									7.73	15	104	7.53	7.34										8.87	15	-353	0.85	6.39			9.31	15	-299	0.72	6.37
									7.55	16	102	6.62	7										8.53	16	-360	0.84	6.41			8.9	16	-306	0.74	6.33
									7.49	17	103	6.23	7										8.37	17	-389	0.83	6.39							
									7.46	18	102	5.89	6.95																					

## Appendix B

Table A-2. Historical Data for Bear Canyon and Woods Canyon Lakes

Site: SW Site ID	Sample: Date	Parameter	Depth	Temp	SpC	DO	DO%	pH	Talk	bicarb	NH3	TKN	NO2+NO3-N	TP	TOC	DOC	hardness	Tca	TMg	TFe	TMn	Chlor-a	Sample: Date	
LCBCL-A	18-Oct-00		0.1	13.62	18.9	6.65	79.8	6.85																
LCBCL-A			1	13.54	18.9	6.6	79	6.75															18-Oct-00	
LCBCL-A			2	13.52	18.8	6.6	78.9	6.69	5.4	6.6	0.15	0.78	0.02	0.012			12			120		1.63	18-Oct-00	
LCBCL-A			5	13.18	18.8	6.58	78.1	6.71															18-Oct-00	
LCBCL-A			6	12.59	18.8	6.4	75	6.67															18-Oct-00	
LCBCL-A			9	12.37	19.1	5.23	60.9	6.57	6.2	7.6	0.17	0.7	<0.01	0.01			10						18-Oct-00	
LCBCL-A			10	11.04	22.1	1.15	13.1	6.12															18-Oct-00	
LCBCL-A			11	8.59	32.4	0.46	4.9	5.8															18-Oct-00	
LCBCL-A		lake in turnover	11.8	8.28	33.3	0.35	3.7	5.82															18-Oct-00	
LCBCL-A	16-May-01	surface warming	0.1	17.03	22	7.87	81.5	7.38															16-May-01	
LCBCL-A			1	17.04	23	7.78	80.5	7.31															16-May-01	
LCBCL-A			2	16.76	23	7.79	80.2	7.28	7	7	0.04	0.69	<0.01	<0.005			20	2.5	0.7	140			16-May-01	
LCBCL-A			3	16.54	22	7.79	79.9	7.26															16-May-01	
LCBCL-A			3.5	12.58	22	8.82	82.9	7.33															16-May-01	
LCBCL-A			4	11.1	22	9.32	84.7	7.2	8	8	0.05	0.62	0.01	<0.005			23	2.4	0.7	100		0.42	16-May-01	
LCBCL-A			5	9.59	22	8.84	77.5	6.93															16-May-01	
LCBCL-A			10	6.47	22	7.5	61	6.43															16-May-01	
LCBCL-A		lake setting up	11.5	5.95	22	7.16	57.4	6.23															16-May-01	
LCBCL-A	13-Jun-01		0.1	18.24	22	8	85	7.02															13-Jun-01	
LCBCL-A			1	18.28	22	7.86	83.5	7.09															13-Jun-01	
LCBCL-A			2	18.22	22	7.8	82.8	7.09	8	8	0.14	0.5	<0.01	0.005			9	2.4	0.7			1.48	13-Jun-01	
LCBCL-A			5	18.14	22	7.76	82.2	7.14															13-Jun-01	
LCBCL-A		lake stratified	6	11.65	21	9.38	86.4	6.94	8	8	0.13	0.56	0.04	0.006	6	6	8	2.6	0.8	30			13-Jun-01	
LCBCL-A			7	9.53	21	8.33	73	6.53															13-Jun-01	
LCBCL-A			8.2	7.76	22	6.28	52.7	6.31															13-Jun-01	
LCBCL-A	18-Sep-01		0.2	19.87	28	7.39	81.1	7.81															18-Sep-01	
LCBCL-A			1.1	19.78	27	7.3	80	7.47															18-Sep-01	
LCBCL-A			2.1	18.38	27	7.32	78	7.35	8	8	0.14	0.49	<0.01	0.005			9	3.9	0.7	30	<	1.38	18-Sep-01	
LCBCL-A			3.2	18.2	27	7.26	77	7.2															18-Sep-01	
LCBCL-A			4	18.16	27	7.26	76.9	7.2															18-Sep-01	
LCBCL-A			5.1	18.05	27	7.07	74.8	7.08															18-Sep-01	
LCBCL-A		lake stratified	6.1	16.81	27	6.26	64.5	6.77															18-Sep-01	
LCBCL-A			7.1	12.89	28	4.54	43	6.36															18-Sep-01	
LCBCL-A			8	9.95	28	1.73	15.3	6.04	7	7	0.13	0.55	<0.01	0.016			10	2.4	0.7	140	30		18-Sep-01	
LCBCL-A			9	8.36	28	0	0	5.92															18-Sep-01	
LCBCL-A			10	7.63	32	0	0	5.96															18-Sep-01	
LCBCL-A	3-May-05		1	15.02		7.88	101	7.65					<0.1	0.45	<0.01	0.06		29.7	8.5	2	511	<		3-May-05
LCBCL-A		still mixed	8	10.4		5.74	66	7.06					0.4	0.57	<0.01	0.07							3-May-05	
LCBCL-A																							3-May-05	
LCBCL-A	30-Aug-05		0					7.9					0.18	1.35	<0.01	0.05		33.1	9.5	2.3	340	151	15.4	30-Aug-05
LCBCL-A			8										1.31	1.9	<0.01	0.49		36.5	11	2.2	1860	785		30-Aug-05
LCBCL-A	17-Nov-05		1	8.74		8.86	99.4	7.91					<0.1	1.77	<0.01	0.17		37.6	11	2.3	737	205	85.1	17-Nov-05
LCBCL-A																							17-Nov-05	
LCBCL-A	22-Oct-09		0.1	11.18	22	7.87	71.7	6.79															22-Oct-09	
LCBCL-A			1	11.18	22	7.84	71.4	6.79															22-Oct-09	
LCBCL-A			2	11.18	22	7.84	71.4	6.84															22-Oct-09	

LCBCL-A			3	11.19	22	7.83	71.3	6.85	8	8	<0.1	0.2	0.02		0.017	7.7	7.5	12	2.4	0.7		5.2	22-Oct-09
LCBCL-A			4	11.18	22	7.83	71.3	6.81															22-Oct-09
LCBCL-A			5	11.18	22	7.83	71.3	6.81															22-Oct-09
LCBCL-A			6	11.17	22	7.83	71.3	6.8															22-Oct-09
LCBCL-A			7	11.17	22	7.82	71.2	6.79															22-Oct-09
LCBCL-A			8	11.17	22	7.83	71.3	6.72															22-Oct-09
LCBCL-A			9	11.17	22	7.83	71.2	6.72															22-Oct-09
LCBCL-A			10	10.73	23	6.74	60.9	6.72															22-Oct-09
LCBCL-A		lake almost turned	11	7.53	29	0.45	3.8	6.23															22-Oct-09
LCBCL-B	18-Oct-00		0.1	13.52	18.7	6.73	80.5	6.08															18-Oct-00
LCBCL-B			1	13.28	18.8	6.65	79.2	6.11															18-Oct-00
LCBCL-B			2	12.85	18.8	6.58	77.6	6.06			0.18	0.95	0.01		0.012				<	<	<	1.01	18-Oct-00
LCBCL-B			5	12.55	18.7	6.45	75.5	6.09															18-Oct-00
LCBCL-B			6	12.54	18.7	6.41	75	6.04															18-Oct-00
LCBCL-B		lake in turnover	8	12.31	18.8	5.91	68.8	6															18-Oct-00

WOODS CANYON

LCWCL-A	19-Oct-94		0.2	10.62	23	7.58	68	7.6																18-Oct-00
LCWCL-A			1.1	10.52	23	7.56	67.6	7.44	11	13.3	0.17	0.81	<0.01		0.027			<	3.1	1	310	70	15.8	19-Oct-94
LCWCL-A			2.1	10.26	23	7.46	66.4	7.38																19-Oct-94
LCWCL-A			3	10.11	23	7.38	65.4	7.36																19-Oct-94
LCWCL-A			4	10.06	23	7.24	64	7.32																19-Oct-94
LCWCL-A			5	10.05	23	7.2	63.7	7.28	11	13.7	0.22	0.65	<0.01		0.018			<	3.1	1	370	80		19-Oct-94
LCWCL-A			6	10.05	23	7.29	64.5	7.17																19-Oct-94
LCWCL-A			7	10.01	23	7.13	63.1	7.15																19-Oct-94
LCWCL-A			8	9.97	23	6.94	61.3	7.12																19-Oct-94
LCWCL-A			9	8.41	41	0.28	2.4	6.49																19-Oct-94
LCWCL-A		lake almost turned	10	7.28	50	0.39	3.2	6.49	17	20.4	0.54	1.11	<0.01		0.054			15	4.1	1.1	5110	430		19-Oct-94
LCWCL-A																								19-Oct-94
LCWCL-A	19-Jun-96		0.4	20.51	22	8.2	91.1	7.01																19-Jun-96
			1	19.96	22	8.22	90.3	7.06	11	13.8								12					1.87	19-Jun-96
			2	19.7	22	8.27	90.4	7.08																19-Jun-96
			3	19.59	22	8.25	90	7.09																19-Jun-96
			4	19.49	22	8.24	89.7	7.06																19-Jun-96
		lake stratified	5	14.61	22	6.97	68.5	6.45	11	13.7								10			120			19-Jun-96
			5.9	13.01	22	4.71	44.7	6.2																19-Jun-96
			7.1	10.81	21	2.11	19	6.01																19-Jun-96
			8	9	24	0.23	2	6.01																19-Jun-96
			9	8.25	29	0.1	0.9	6.03																19-Jun-96
			10	7.98	32	0.19	1.6	6.06	14	16.6								17			2240	310		19-Jun-96
			10.7	7.84	35	0.14	1.1	6.1																19-Jun-96
LCWCL-A	19-Oct-00		0.1	13.67	30.5	7.35	88.2	6.42																19-Oct-00

LCWCL-A	16-May-01	1	13.42	30.4	7.29	87.1	6.46	13	16	0.16	0.86	0.01	0.013	17	<	1.2	200	51	0.58	19-Oct-00											
		2	13.26	30.4	7.26	86.3	6.44													19-Oct-00											
		5	12.98	30.3	7.07	83.6	6.4													19-Oct-00											
		6	12.86	30.4	6.93	81.7	6.44													19-Oct-00											
		8.1	10.91	39.4	0.72	8.2	5.76													19-Oct-00											
		9.2	7.91	53.5	0.43	4.5	5.89	15	18	0.15	0.82	<0.01	0.03	19	<	1.2	4300	680	19-Oct-00												
		0.1	18.45	27	7.58	80.8	7.38	11	11	0.05	0.8	0.01	<0.005	34	3.2	0.9	90	<	0.55	16-May-01											
		1	18.44	27	7.42	79	7.26													16-May-01											
		2	18.03	27	7.4	78.2	7.25													16-May-01											
		3	17.84	27	7.4	77.9	7.23													16-May-01											
3.5	10.87	26	9.42	85.2	7.12	16-May-01																									
4	9.43	26	9.48	82.8	7.1	16-May-01																									
5	8.19	26	9.14	77.6	6.99	16-May-01																									
6	6.83	26	8.65	71	6.89	11	11													0.04	0.6	0.01	<0.005	17	3.2	0.9	230	20	2.06	16-May-01	
10.1	5.82	27	6.04	48.3	6.58	16-May-01																									
LCWCL-A	12-Jun-01	0.1	20.16	27	7.67	84.7	7.69													12-Jun-01											
		0.5	20.16	27	7.11	78.4	7.4	12-Jun-01																							
		1	20.17	27	7.03	77.6	7.32	12-Jun-01																							
		2.5	19.94	27	6.94	76.3	7.29	12-Jun-01																							
		LCWCL-A	18-Sep-01	0.1	19.82	35	7.13	78.1	7.48	14	14	0.13	0.47	<0.01	0.013	21	5.6	1	60		10	1.9	18-Sep-01								
1.1	19.33			35	7.12	77.3	7.36	18-Sep-01																							
3.1	19.08			35	7.09	76.5	7.27	18-Sep-01																							
4.9	18.7			35	5.87	62.9	7.04	18-Sep-01																							
6	16.24			37	2.81	28.6	6.6	18-Sep-01																							
7	12.63			38	0.27	2.5	6.34	14	14											0.1			0.6	<0.01	0.02	14	6.1	1.1	270	130	18-Sep-01
7.9	9.1			44	0.08	0.7	6.24	18-Sep-01																							
9.1	7.81			53	0.04	0.3	6.19	18-Sep-01																							
LCWCL-A	22-May-02	1	15.42	26	7.89	106	8.14	9.4	0.42	<0.01	12.2	3.3	1	101	<	22-May-02															
		7	9	24.9	5.5	63.8	7.67	12									0.41	<0.01	12.1	3.4	0.9	263	<	22-May-02							
LCWCL-A	16-Jul-02	1	20.87	28.2	6.15	92	8	0.33	<0.01	<0.005	14.7	4.2	1	<	<	16-Jul-02															
		7	11.18	27.6	0.14	1.2	7.37										0.4	<0.01	0.24	15.3	4.5	1	304	121	16-Jul-02						
LCWCL-A	28-Oct-02	1	11.28	30.5	6.16	78.4	7.7	0.14	<0.01	0.01	28-Oct-02																				
LCWCL-A	11-Apr-03	1	8.56	22	9.15	104	6.78					11	<0.1	<0.01	10.7	2.9	0.8	127	<	4.4	11-Apr-03										
LCWCL-A	23-Jul-03	1	22.13	28	6.6	99	7.06	5	<0.1	0.41	<0.01	2.9	0.9	<	<	3.4	23-Jul-03														
		8	8.09	34	0.35	8	5.78	11										<0.1	0.51	<0.01	3.4	0.9	1770	334	23-Jul-03						
LCWCL-A	20-Oct-03	1	15.29	27	5.94	77	7.14	11	<0.1	0.38	3	20-Oct-03																			
LCWCL-A	14-May-04	1	16.62	25.9	7.25	98	7.53	12	<0.1	0.31	<0.01	4.43	14-May-04																		
		9	5.82	27.5	0.46	5	6.52	11						0.36	<0.01	14-May-04															
LCWCL-A	19-Aug-04	1	19.18	28	5.5	78	7.44	17	<0.1	0.4	<0.01	19-Aug-04																			
		8	7.68	42.6	0.39	4	8.48	15					<0.1	0.65	<0.01	19-Aug-04															

LCWCL-A	2-Nov-04	1	8.41	29	7.64	84.7	6.86	13												2-Nov-04
LCWCL-A	3-May-05	1	13		8.31	83	7.7		<0.1	0.32	<0.01	0.01		9.74	2.3	<	246	<		3-May-05
		9	5.08		5.44	45	6.53		0.13	0.37	<0.01	0.01								3-May-05
LCWCL-A	30-Aug-05	1	21.76		6.41	96	7.4		<0.1	0.32	<0.01	<0.005		12.2	3.2	<	<	<	1.67	30-Aug-05
		8	7.45		0.26	3	5.91		0.12	0.49	<0.01	0.03		14.7	4.2	<	2830	497		30-Aug-05
LCWCL-A	17-Nov-05	1	8.21		6.87	76	7.07		<0.1	0.43	<0.01	<0.005		18.3	5.7	<	872	145	11.61	17-Nov-05
LCWCL-B	19-Oct-94	0.1	11.79	23	8.06	74.2	7.16													19-Oct-94
		1	11.63	23	7.64	70.1	7.11													19-Oct-94
		2	10.27	23	7.81	69.4	7.1													19-Oct-94
		3	10.17	23	7.64	67.8	7.07													19-Oct-94
		4	10.13	23	7.49	66.4	7.02													19-Oct-94
		5	10.06	23	7.38	65.3	6.99													19-Oct-94
		6	10.06	23	7.36	65.2	6.98													19-Oct-94
		7	10.03	23	7.09	62.7	6.96													19-Oct-94
		8	9.7	23	6.02	52.8	6.85													19-Oct-94
LCWCL-B	19-Oct-00	0.1	13.46	30.4	7.33	87.5	6.38													19-Oct-00
		2	13.26	30.3	7.29	86.7	6.35	13	16	0.15	0.79	<0.01	0.013	16		1.3	100	55	0.93	19-Oct-00
		5	12.96	30.3	6.98	82.5	6.28													19-Oct-00
		5.9	12.88	30.4	6.38	75.2	6.28													19-Oct-00
LCWCL-B	12-Jun-01	0.1	19.84	27	6.98	76.5	7.66												12-Jun-01	
1		19.88	27	6.87	75.4	7.58													12-Jun-01	
2		19.54	27	6.86	74.8	7.57	13	13	0.09	0.6	0.04	0.009	11						12-Jun-01	
3		18.88	27	6.85	73.6	7.41													12-Jun-01	
4		16.26	26	7.19	73.3	7.31													12-Jun-01	
5		12.65	26	8.02	75.5	7.19	11	11	0.13	0.62	0.03	0.023	11						12-Jun-01	
LCWCL-B		6	8.44	27	5.48	46.8	6.89												12-Jun-01	

BCL = Bear Canyon Lake

WCL = Woods Canyon Lake

	hypoxia to anoxia
	below WQS
	above WQS (although total, not dissolved)
	above target